Supporting Information for

# Conformational Preferences of *cis*–1,3–Cyclopentanedicarboxylic Acid and its Salts by 1H NMR Spectroscopy: Energetics of Intramolecular Hydrogen Bonds in DMSO

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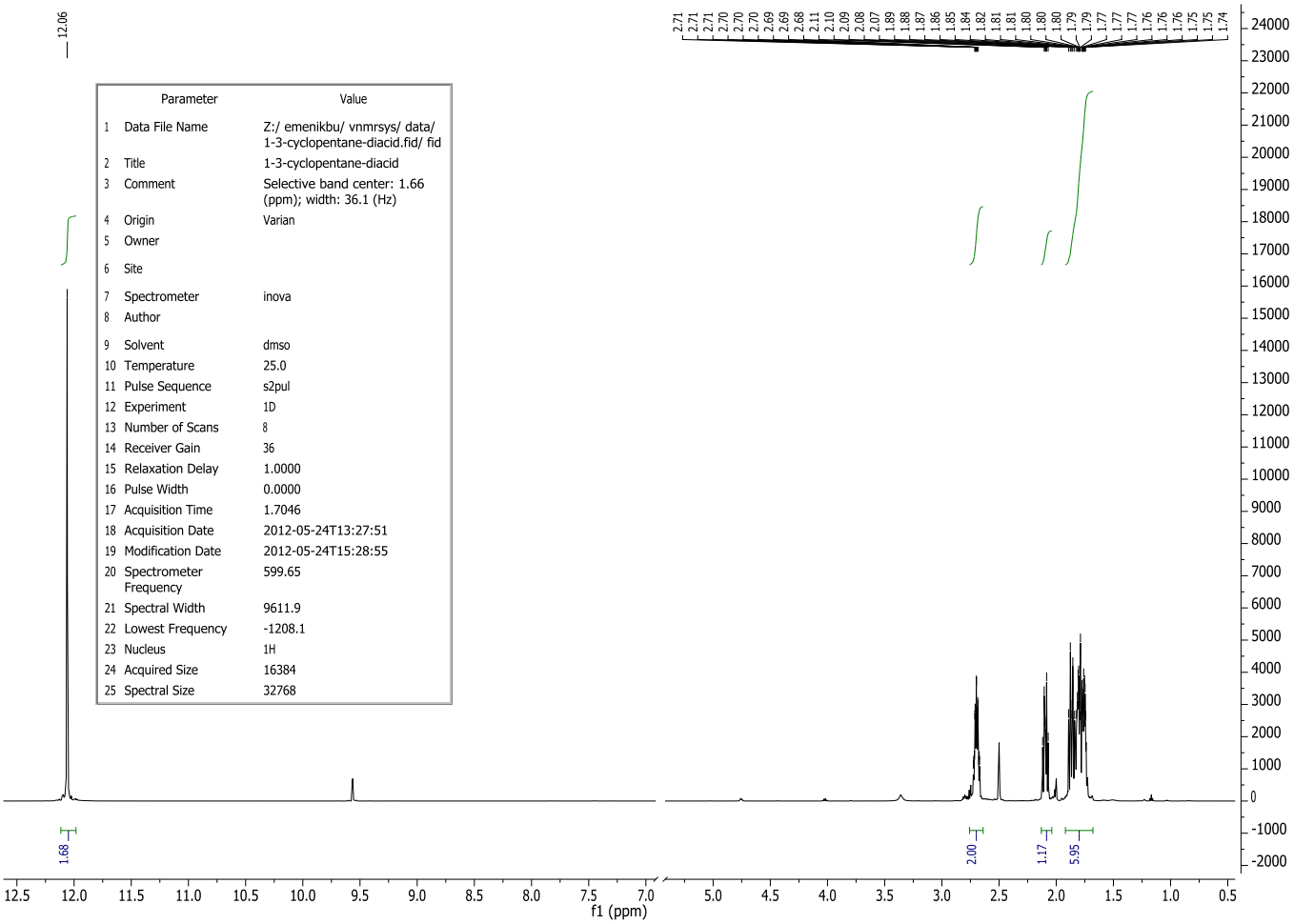
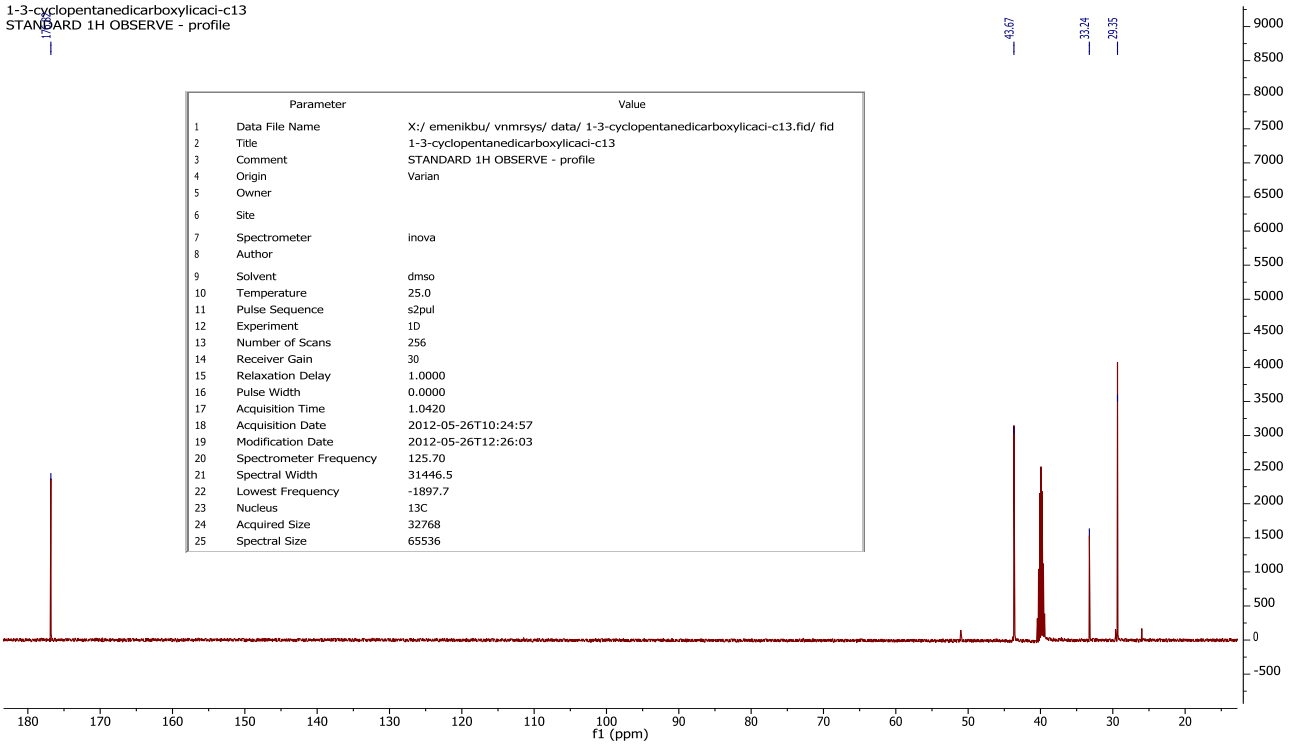
## Proton NMR spectra of *cis*-1,3-cyclopentanedicarboxylic acid in DMSO-$d_6$



## Carbon NMR spectra of *cis*-1,3-cyclopentanedicarboxylic acid in DMSO-d$_6$




| | Parameter | Value |
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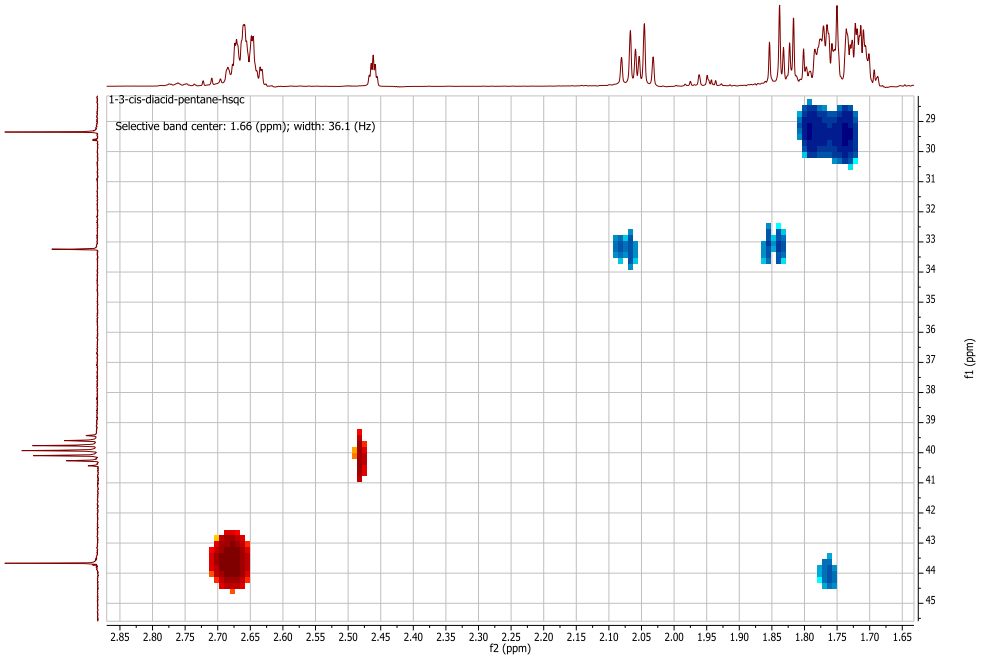
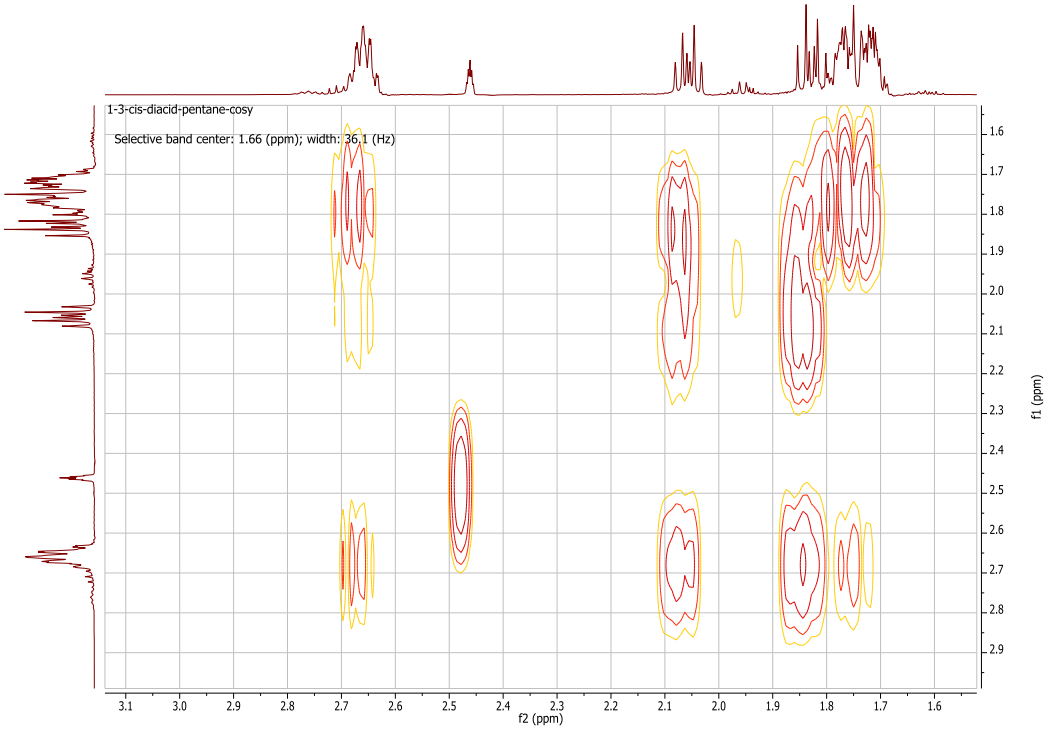
| 1 | Data File Name | X:/ emenikbu/ vnmrsys/ data/ 1-3-cyclopentanedicarboxylicaci-c13.fid/ fid |
| 2 | Title | 1-3-cyclopentanedicarboxylicaci-c13 |
| 3 | Comment | STANDARD 1H OBSERVE - profile |
| 4 | Origin | Varian |
| 5 | Owner | |
| 6 | Site | |
| 7 | Spectrometer | inova |
| 8 | Author | |
| 9 | Solvent | dmso |
| 10 | Temperature | 25.0 |
| 11 | Pulse Sequence | s2pul |
| 12 | Experiment | 1D |
| 13 | Number of Scans | 256 |
| 14 | Receiver Gain | 30 |
| 15 | Relaxation Delay | 1.0000 |
| 16 | Pulse Width | 0.0000 |
| 17 | Acquisition Time | 1.0420 |
| 18 | Acquisition Date | 2012-05-26T10:24:57 |
| 19 | Modification Date | 2012-05-26T12:26:03 |
| 20 | Spectrometer Frequency | 125.70 |
| 21 | Spectral Width | 31446.5 |
| 22 | Lowest Frequency | -1897.7 |
| 23 | Nucleus | 13C |
| 24 | Acquired Size | 32768 |
| 25 | Spectral Size | 65536 |

## HSQC NMR spectra of *cis*-1,3-cyclopentanedicarboxylic acid in DMSO-d$_6$

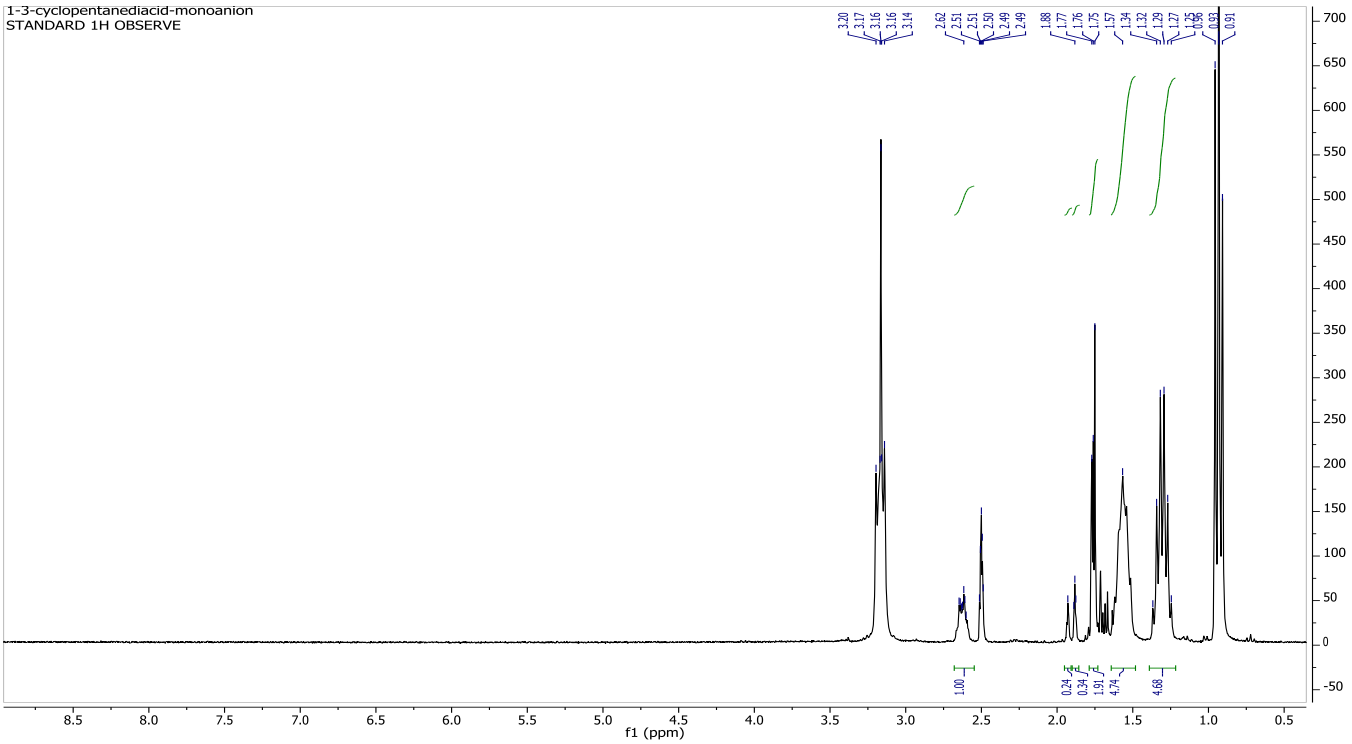



C

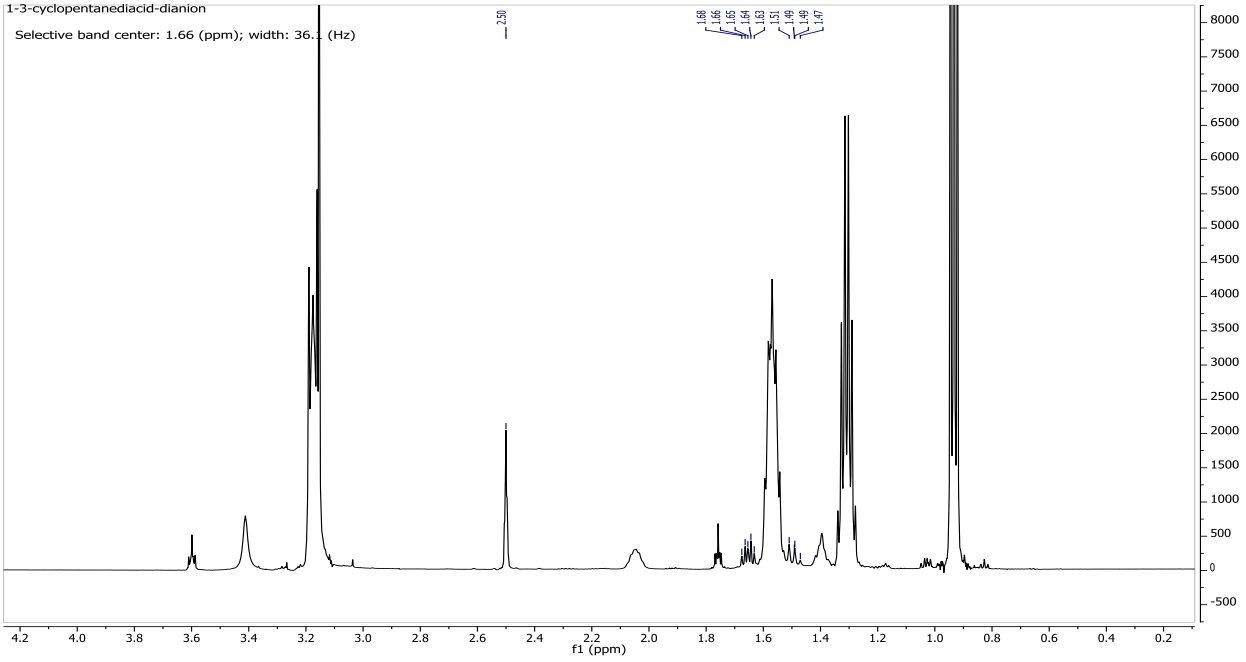
**COSY NMR spectra of *cis*-1,3-cyclopentanedicarboxylic acid in DMSO-d$_6$**

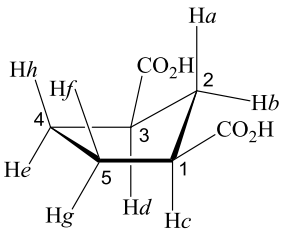



**PROTON NMR spectra of *cis*-1,3-cyclopentanedicarboxylic monoanion in DMSO-d$_6$**
(counter ion: tetrabutyl ammonium)



**PROTON NMR spectra of *cis*-1,3-cyclopentanedicarboxylic dianion in DMSO-d$_6$**
(counter ion: tetrabutyl ammonium)




**1**

Coupling Constants Generated by gNMR Simulation for **1**

*Geminal Couplings* (Hz):

$^2J_{ab}$ = -12.95 $^2J_{eh}$ = -15.83 $^2J_{fg}$ = -9.41

*Vicinal Couplings* (Hz):

$^3J_{ac}$ = 8.01 $^3J_{ad}$ = 8.20 $^3J_{bc}$ = 9.36 $^3J_{bd}$ = 9.20

$^3J_{ef}$ = 6.55 $^3J_{gh}$ = 6.59 $^3J_{eg}$ = 7.76 $^3J_{fh}$ = 7.63

*Long-range Couplings* (Hz):

$^4J_{af}$ = -0.15 $^4J_{cd}$ = 0.09 $^4J_{ah}$ = 0.71

$^4J_{bf}$ = 0.10 $^4J_{ag}$ = 0.22 $^4J_{eh}$ = -0.45

$^4J_{bh}$ = 0.28 $^4J_{bg}$ = -0.21 $^4J_{be}$ =-0.26

## GNMR SIMULATED SPECTRA

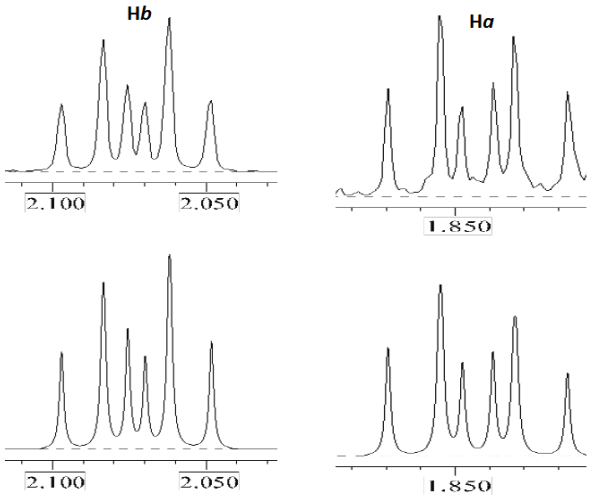



**Figure S1**: The simulated (bottom) and experimental $^{1}$H NMR spectra (top) of cis-1,3-cyclopentanedicarboxylic acid, showing $H_{a,}$and $H_b$ peaks

| # | Nucleus | n | Shift | Width | J[1] | J[2] | J[3] |
|---|---|---|---|---|---|---|---|
| 1 | 1H | 1 | 2.072 | | | | |
| | | | a | - | | | |
| 2 | 1H | 1 | 1.844 | | -12.95 | | |
| | | | b | - | ab | | |
| 3 | 1H | 1 | 2.700 | | 8.01 | 9.36 | |
| | | | c | - | ac | bc | |
| 4 | 1H | 1 | 2.700 | | 8.20 | 9.20 | 0.09 |
| | | | d | - | ad | bd | cd |

**Figure S2**: The chemicals shifts and coupling constants for the computed $^{1}$H NMR spectrum of cis-1,3-cyclopentanedicarboxylic acid ($H_{a,}$and $H_b$ peaks)

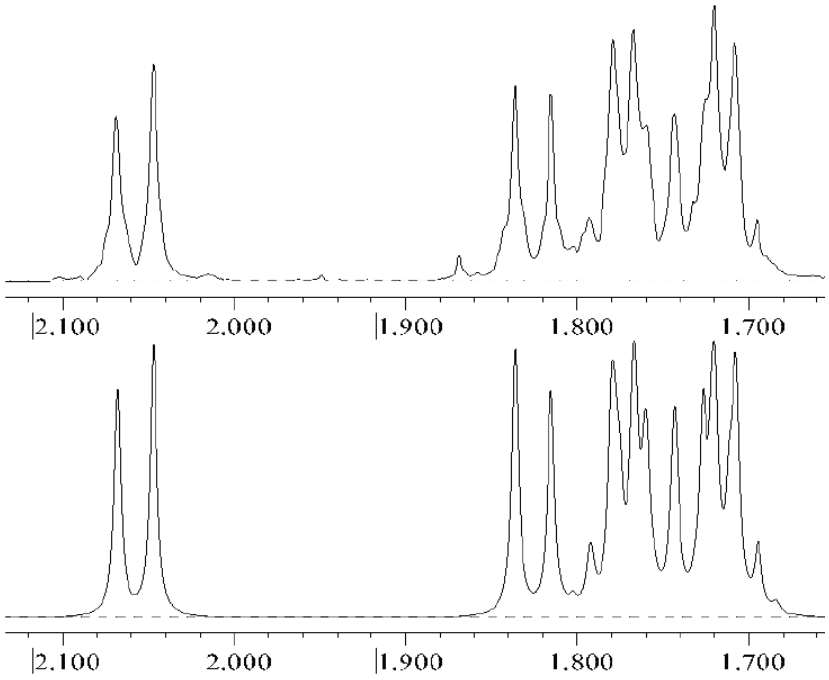



**Figure S3**: The simulated (bottom) and experimental (top) $^{1}$H NMR spectra of cis-1,3-cyclopentanedicarboxylic acid (decoupled at $H_{c,d}$ peaks)

| # | Nucleus | n | Shift | Width | J[1] | J[2] | J[3] | J[4] | J[5] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1H | 1 | 1.716 | | | | | | |
| | | | e | - | | | | | |
| 2 | 1H | 1 | 1.773 | | 6.55 | | | | |
| | | | f | - | ef | | | | |
| 3 | 1H | 1 | 1.714 | | 7.76 | -9.41 | | | |
| | | | g | - | eg | fg | | | |
| 4 | 1H | 1 | 1.771 | | -15.83 | 7.63 | 6.59 | | |
| | | | h | - | eh | fh | gh | | |
| 5 | 1H | 1 | 1.826 | | -0.45 | -0.15 | 0.22 | 0.71 | |
| | | | a | - | ea | fa | ga | ha | |
| 6 | 1H | 1 | 2.057 | | -0.26 | 0.10 | -0.21 | 0.28 | -12.49 |
| | | | b | - | eb | fb | gb | hb | ab |

**Figure S4**: The chemicals shifts and coupling constants for the computed $^{1}$H NMR spectrum of cis-1,3-cyclopentanedicarboxylic acid (decoupled at $H_{c,d}$ peaks)

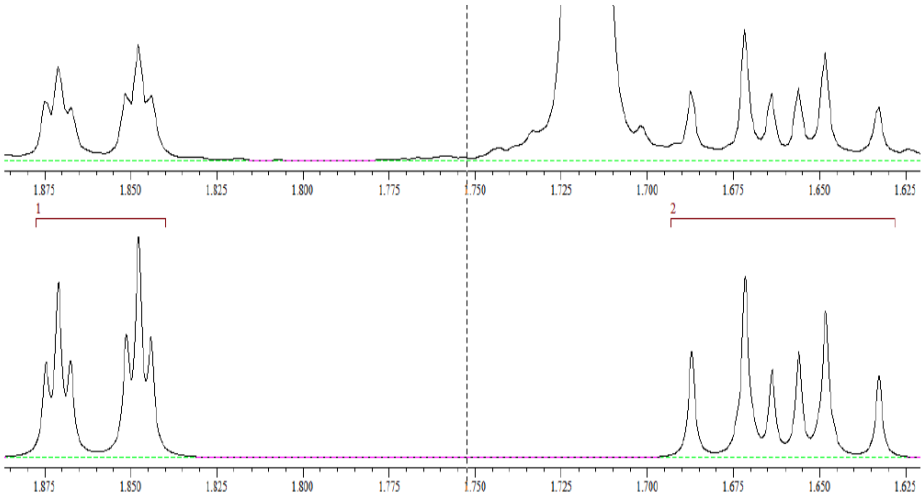



**Figure S5**: The simulated (bottom) and experimental $^{1}$H NMR spectra (top) of cis-1,3-cyclopentanedicarboxylic acid monoanion, showing $H_{a,}$and $H_b$ peaks

| # | Nucleus | n | Shift | Width | J[1] | J[2] | J[3] |
|---|---|---|---|---|---|---|---|
| 1 | 1H | 1 | 1.859 | | | | |
| | | | a | - | | | |
| 2 | 1H | 1 | 1.661 | | -13.99 | | |
| | | | b | - | ab | | |
| 3 | 1H | 1 | 0.000 | | 2.40 | 9.87 | |
| | | | c | - | ac | bc | |
| 4 | 1H | 1 | 0.000 | | 0.98 | 8.83 | -1.28 |
| | | | d | - | ad | bd | cd |

**Figure S6**: The chemicals shifts and coupling constants for the computed $^{1}$H NMR spectrum of cis-1,3-cyclopentanedicarboxylic acid monoanion ($H_{a,}$and $H_b$ peaks)

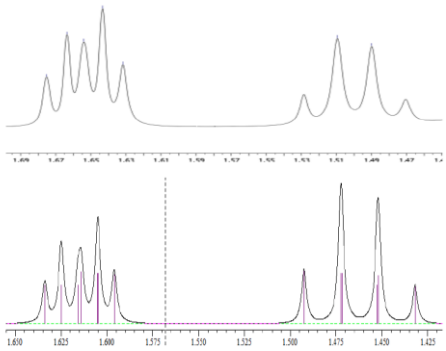


**Figure S7**: The simulated (bottom) and experimental $^{1}$H NMR spectra (top) of cis-1,3-cyclopentanedicarboxylic acid dianion, showing $H_{a,}$and $H_b$ peaks (*the -$CH_2$ counter ion peak of the N-butyl group at 1.55 ppm were suppressed using Mestrenova software*)

| # | Nucleus | n | Shift | Width | J[1] | J[2] | J[3] | J[4] | J[5] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1H | 1 | 1.463 | | | | | | |
| | | | a | - | | | | | |
| 2 | 1H | 1 | 1.614 | | -11.95 | | | | |
| | | | b | - | ab | | | | |
| 3 | 1H | 1 | 2.504 | | 12.35 | 4.99 | | | |
| | | | c | - | ac | - bc | | | |
| 4 | 1H | 1 | 2.498 | | 12.10 | 5.77 | -11.20 | | |
| | | | d | - | ad | -bd | cd | | |
| 5 | 1H | 1 | 2.600 | | 0.00 | 0.00 | 0.00 | 0.00 | |
| | | | e | - | ae | be | ce | de | |
| 6 | 1H | 1 | 0.000 | | 0.00 | -0.00 | -0.00 | 0.00 | 0.00 |
| | | | - | - | af | bf | cf | df | ef |

**Figure S8**: The chemicals shifts and coupling constants for the computed $^{1}$H NMR spectrum of cis-1,3-cyclopentanedicarboxylic acid dianion ($H_a$,and $H_b$ peaks)

## CARTESIAN COORDINATES OF OPTMIZED GEOMETRIES AT B3LYP/6–31G(2d,2p) (IEF-PCM = DMSO)

**Table S1:**Cartesian coordinates of *cis*-1,3-cyclopentanedicarboxylic acid (Conformer 1**(***eaZZ***)**)

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.714808 | 1.682027 | -0.112848 |
| 2 | 6 | 0 | 1.240756 | 0.316362 | -0.632646 |
| 3 | 6 | 0 | -1.192265 | 0.217856 | -0.466779 |
| 4 | 6 | 0 | -0.725522 | 1.430791 | 0.376784 |
| 5 | 1 | 0 | 1.346862 | 2.080925 | 0.680869 |
| 6 | 1 | 0 | 0.716737 | 2.403937 | -0.932205 |
| 7 | 1 | 0 | -0.726794 | 1.151283 | 1.434824 |
| 8 | 1 | 0 | -1.373696 | 2.300380 | 0.257071 |
| 9 | 6 | 0 | 0.050892 | -0.684999 | -0.486300 |
| 10 | 1 | 0 | 0.112882 | -1.221090 | 0.464421 |
| 11 | 1 | 0 | 0.032088 | -1.423062 | -1.288711 |
| 12 | 1 | 0 | 1.511437 | 0.387331 | -1.687718 |
| 13 | 1 | 0 | -1.431890 | 0.557557 | -1.477605 |
| 14 | 6 | 0 | -2.417858 | -0.440246 | 0.117647 |
| 15 | 8 | 0 | -2.423188 | -1.240136 | 1.029746 |

| | | | | | |
|---|---|---|---|---|---|
| 16 | 8 | 0 | -3.554706 | -0.010949 | -0.467697 |
| 17 | 1 | 0 | -4.303577 | -0.436893 | -0.019369 |
| 18 | 6 | 0 | 2.454308 | -0.204624 | 0.100901 |
| 19 | 8 | 0 | 2.834332 | 0.142541 | 1.198878 |
| 20 | 8 | 0 | 3.085891 | -1.167454 | -0.603857 |
| 21 | 1 | 0 | 3.826605 | -1.495386 | -0.068683 |

**Table S2:** Cartesian coordinates of *cis*-1,3-cyclopentanedicarboxylic acid (Conformer 1′**(***aeZZ***)**)

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.664927 | 1.521787 | -0.655368 |
| 2 | 6 | 0 | 0.800694 | 1.895200 | -0.358977 |
| 3 | 6 | 0 | 0.122011 | 0.428465 | 1.440200 |
| 4 | 6 | 0 | -1.137625 | 0.671219 | 0.577328 |
| 5 | 1 | 0 | -1.299388 | 2.395812 | -0.804683 |
| 6 | 1 | 0 | -0.713102 | 0.924040 | -1.567554 |
| 7 | 6 | 0 | 1.328919 | 0.755419 | 0.522472 |
| 8 | 1 | 0 | 1.385790 | 2.026866 | -1.270171 |
| 9 | 1 | 0 | 0.159607 | -0.583230 | 1.842169 |
| 10 | 1 | 0 | 0.848969 | 2.827023 | 0.211285 |
| 11 | 1 | 0 | 0.126773 | 1.125430 | 2.280279 |
| 12 | 1 | 0 | 2.194112 | 1.048230 | 1.122460 |
| 13 | 1 | 0 | -1.897804 | 1.219298 | 1.136510 |
| 14 | 6 | 0 | 1.750123 | -0.454069 | -0.289431 |
| 15 | 8 | 0 | 1.602724 | -0.601469 | -1.481938 |
| 16 | 8 | 0 | 2.340913 | -1.385717 | 0.486341 |
| 17 | 1 | 0 | 2.565406 | -2.134723 | -0.087489 |
| 18 | 6 | 0 | -1.772483 | -0.615139 | 0.101506 |
| 19 | 8 | 0 | -1.256372 | -1.710847 | 0.110734 |
| 20 | 8 | 0 | -3.011059 | -0.403332 | -0.386990 |
| 21 | 1 | 0 | -3.340283 | -1.255128 | -0.714365 |

**Table S3:** Cartesian coordinates of *cis*-1,3-cyclopentanedicarboxylic acid (Conformer 1**(***eeZZ***)**)

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.839259 | 1.580107 | -0.302081 |
| 2 | 6 | 0 | -0.525961 | 1.140392 | -0.842988 |
| 3 | 6 | 0 | -0.039257 | -0.317285 | 1.034711 |
| 4 | 6 | 0 | 1.267249 | 0.430024 | 0.669389 |
| 5 | 1 | 0 | 1.572933 | 1.767246 | -1.088121 |
| 6 | 1 | 0 | 0.733138 | 2.505150 | 0.270091 |
| 7 | 6 | 0 | -1.188942 | 0.483861 | 0.392795 |
| 8 | 1 | 0 | -1.112664 | 1.964418 | -1.252610 |
| 9 | 1 | 0 | -0.164210 | -0.418671 | 2.113547 |
| 10 | 1 | 0 | -0.401258 | 0.387621 | -1.628516 |
| 11 | 1 | 0 | -0.018378 | -1.317830 | 0.600635 |
| 12 | 1 | 0 | 1.757262 | 0.858073 | 1.545056 |
| 13 | 1 | 0 | -1.539330 | 1.274407 | 1.060921 |
| 14 | 6 | 0 | -2.375105 | -0.365203 | 0.001779 |
| 15 | 8 | 0 | -2.328488 | -1.522309 | -0.351623 |
| 16 | 8 | 0 | -3.527938 | 0.332394 | 0.048174 |
| 17 | 1 | 0 | -4.233735 | -0.260254 | -0.255617 |
| 18 | 6 | 0 | 2.283299 | -0.470453 | -0.003548 |
| 19 | 8 | 0 | 2.065512 | -1.546637 | -0.512907 |
| 20 | 8 | 0 | 3.508808 | 0.093885 | -0.006143 |
| 21 | 1 | 0 | 4.099846 | -0.507497 | -0.485726 |

**Table S4:** Cartesian coordinates of *cis*-1,3-cyclopentanedicarboxylic acid (Conformer 1′**(***eeZZ***)**)

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.776989 | 1.352410 | 0.656545 |
| 2 | 6 | 0 | -1.198592 | 0.302915 | -0.419836 |
| 3 | 6 | 0 | 1.198603 | 0.303021 | -0.419672 |
| 4 | 6 | 0 | 0.776810 | 1.352218 | 0.656889 |
| 5 | 1 | 0 | -1.191955 | 2.334914 | 0.429256 |
| 6 | 1 | 0 | -1.152904 | 1.056644 | 1.638539 |
| 7 | 1 | 0 | 1.192132 | 2.334711 | 0.430198 |
| 8 | 1 | 0 | 1.152210 | 1.055916 | 1.638919 |
| 9 | 6 | 0 | 0.000050 | -0.650516 | -0.506023 |
| 10 | 1 | 0 | 0.000133 | -1.249848 | -1.418822 |
| 11 | 1 | 0 | 0.000035 | -1.330864 | 0.348829 |
| 12 | 6 | 0 | 2.500756 | -0.367699 | -0.059926 |
| 13 | 8 | 0 | 2.621251 | -1.373952 | 0.606736 |

| | | | | | |
|---|---|---|---|---|---|
| 14 | 8 | 0 | 3.566818 | 0.306474 | -0.539664 |
| 15 | 1 | 0 | 4.370439 | -0.148078 | -0.238672 |
| 16 | 6 | 0 | -2.500708 | -0.367854 | -0.060056 |
| 17 | 8 | 0 | -2.621150 | -1.374496 | 0.606027 |
| 18 | 8 | 0 | -3.566821 | 0.306769 | -0.539057 |
| 19 | 1 | 0 | -4.370415 | -0.147836 | -0.238076 |
| 20 | 1 | 0 | -1.338102 | 0.814414 | -1.375144 |
| 21 | 1 | 0 | 1.338078 | 0.814697 | -1.374888 |

**Table S5:** Cartesian coordinates of *cis*-1,3-cyclopentanedicarboxylic acid monoanion (Conformer **1A**)

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.019976 | 1.666252 | -0.549522 |
| 2 | 6 | 0 | -1.329500 | 0.670068 | 0.595475 |
| 3 | 6 | 0 | 1.144910 | 0.830401 | 0.268944 |
| 4 | 6 | 0 | 0.392713 | 1.284319 | -1.023984 |
| 5 | 1 | 0 | -1.759500 | 1.639170 | -1.353457 |
| 6 | 1 | 0 | -1.015676 | 2.682274 | -0.140528 |
| 7 | 1 | 0 | 0.334537 | 0.461234 | -1.740582 |
| 8 | 1 | 0 | 0.910246 | 2.108874 | -1.518173 |
| 9 | 6 | 0 | 0.024977 | 0.567737 | 1.329122 |
| 10 | 1 | 0 | 0.148796 | -0.385188 | 1.846823 |
| 11 | 1 | 0 | 0.077572 | 1.351792 | 2.088290 |
| 12 | 1 | 0 | -2.105341 | 1.069766 | 1.250824 |
| 13 | 1 | 0 | 1.798480 | 1.631340 | 0.613192 |
| 14 | 6 | 0 | -1.869713 | -0.658754 | 0.035908 |
| 15 | 6 | 0 | 2.051017 | -0.362756 | 0.012523 |
| 16 | 8 | 0 | -3.105379 | -0.771624 | -0.099286 |
| 17 | 8 | 0 | 3.273000 | -0.269932 | 0.024065 |
| 18 | 8 | 0 | 1.466652 | -1.520727 | -0.241503 |
| 19 | 8 | 0 | -1.031224 | -1.571608 | -0.287045 |
| 20 | 1 | 0 | 0.419935 | -1.471744 | -0.227037 |

**Table S6:** Cartesian coordinates of *cis*-1,3-cyclopentanedicarboxylic acid dianion (Conformer **1B**)

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 1.217485 | 0.174719 | -0.536903 |
| 2 | 6 | 0 | 0.019492 | -0.733445 | -0.178828 |
| 3 | 6 | 0 | -0.785573 | 1.521743 | 0.072641 |
| 4 | 6 | 0 | 0.763669 | 1.581282 | -0.063319 |
| 5 | 1 | 0 | 1.322669 | 0.177403 | -1.625990 |
| 6 | 1 | 0 | 1.228590 | 1.810646 | 0.897823 |
| 7 | 1 | 0 | 1.081932 | 2.351595 | -0.771853 |
| 8 | 6 | 0 | -1.207744 | 0.141097 | -0.488137 |
| 9 | 1 | 0 | -1.314115 | 0.217110 | -1.575461 |
| 10 | 1 | 0 | 0.024649 | -1.676503 | -0.734465 |
| 11 | 1 | 0 | -1.286097 | 2.342651 | -0.448784 |
| 12 | 6 | 0 | -2.548799 | -0.376979 | 0.072452 |
| 13 | 8 | 0 | -2.606956 | -0.637997 | 1.305744 |
| 14 | 8 | 0 | -3.505928 | -0.495588 | -0.747216 |
| 15 | 6 | 0 | 2.553271 | -0.333045 | 0.048056 |
| 16 | 8 | 0 | 2.759134 | -0.164967 | 1.281471 |
| 17 | 8 | 0 | 3.342950 | -0.912292 | -0.754094 |
| 18 | 1 | 0 | 0.034553 | -0.968217 | 0.890265 |
| 19 | 1 | 0 | -1.076582 | 1.579851 | 1.125453 |